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Low-Temperature Raman Scattering Spectra of $GaSe_xS_{1-x}$ Layered Mixed Crystals

Raman scattering has been used to study the vibrational spectra of $GaSe_xS_{1-x}$ layered mixed crystals at 10 K. We report the frequency dependencies of different modes on composition x , with particular emphasis on $A_1^{\prime(2)}$ (A_{1g}^1) and $A_1^{\prime(4)}$ (A_{1g}^2) intralayer compressional modes having low dispersion in the Brillouin zone. The appearance of additional bands is attributed to multimode behavior typically exhibited by mixed crystals of anisotropic compounds.

Keywords: Raman scattering, layered mixed crystals, $GaSe_xS_{1-x}$

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1. Introduction

GaS and GaSe are layered compounds, in which bonds within the layers are considerably stronger than those perpendicular to the layers. Their structures may be considered as two-dimensional, as a consequence of strong ionic-covalent intralayer and weak van der Waals interlayer interactions. The distinctive interatomic forces in layered structures manifest themselves with typical features in their phonon spectra, for example weak dispersion of phonon branches in some directions in the Brillouin zone and low-frequency interlayer modes.

The layer compounds GaS and GaSe form a series of $GaSe_xS_{1-x}$ mixed crystals with no restrictions on the concentrations of the components: $0 \le x \le 1$ (MASUI et al.; OSMAN). The phonon spectra of $GaSe_xS_{1-x}$ mixed crystals at room temperature have been deduced previously from Raman and Brillouin scattering (HAYEK et al.; MERCIER, VOITCHOVSKY; GASANLY et al.; YAMADA et al.) and infrared reflection (RIEDE et al.; GASANLY et al.) measurements.

We present in this paper for the first time the experimental results on Raman scattering from $GaSe_xS_{1-x}$ mixed crystals at T = 10 K. We report the frequency shifts of different modes, in particular the $A_1^{\prime(2)}$ (A_{1g}^1) and $A_1^{\prime(4)}$ (A_{1g}^2) intralayer compressional modes, with composition of the mixed crystals. The appearance of additional bands in the region 135-190 cm^{-1} is attributed to multimode behavior typical for mixed crystals of anisotropic compouds. We discuss anomalies observed in the spectra for the intralayer $A_1^{\prime(2)}$ (A_{1g}^1) compressional modes due to polytype transformations.

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2. Crystal symmetry and group-theoretical analysis

The $GaSe_xS_{1-x}$ mixed crystals, like the pure compounds GaS and GaSe, have a layered structure. Each of the layers comprises four atomic planes with the sequence S(Se) - Ga - Ga - S(Se). Depending on the layer stacking, polytypes ε , β, and γ are distinguished (KUHN et al. 1975, 1976). Figure 1 shows schematically the stacking arrangement of two neighboring layers in the ε- and β-polytypes. GaSe crystals grown from the melt by the Bridgman method present only the parallel ε-polytype whereas GaS crystals invariably present the antiparallel β modification, which is also sometimes found in vapor-grown GaSe. The $GaSe_xS_{1-x}$ mixed crystals change their polytype ($\beta \rightarrow \varepsilon$) with increase of x from 0 to 1: for $0 \le x \le 0.4$ and $0.6 \le x \le 1$ the β- and ε-polytypes predominate, respectively; for intermediate region the mixture of two polytypes occurs (KYAZYMZADE et al.).

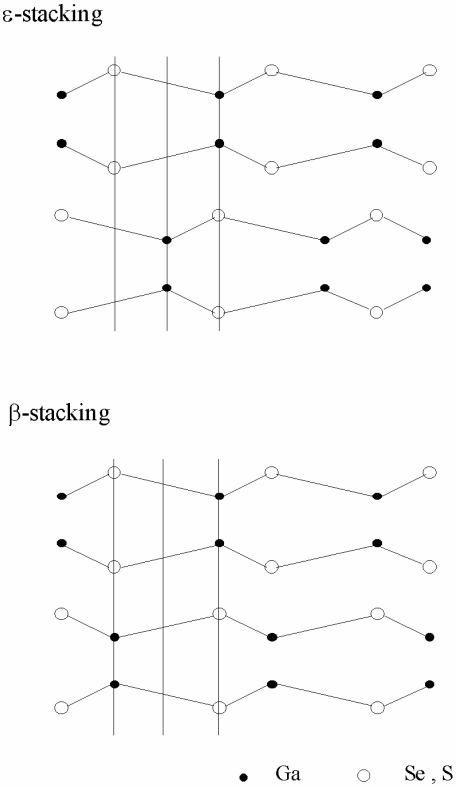

Fig. 1: Stacking sequences for ε- and β-polytypes of GaSe and GaS crystals.

The space group of β-GaS and ε-GaSe crystals are D_{6h}^4 and D_{3h}^1, respectively (HAYEK et al.). In the β- and ε-type structures, the primitive hexagonal unit cell consists of four formula units from two neighboring layers. For GaS, there are 24 normal modes of vibration at the center of the Brillouin zone and these can be described by the irreducible representations of the D_{6h} point group

$$\Gamma \equiv 2A_{1g} + 2A_{2u} + 2B_{1u} + 2B_{2g} + 2E_{1g} + 2E_{1u} + 2E_{2g} + 2E_{2u}.$$

Thus, there are six Raman-active modes ($2A_{1g} + 2E_{1g} + 2E_{2g}$) and two infrared-active modes ($E_{1u} + A_{2u}$).

For ε-polytype of GaSe, 24 normal modes are given by the irreducible representations of the D_{3h} point group

$$\Gamma \equiv 4\,A_1' + 4\,A_2'' + 4E' + 4E''.$$

In this case, there are eleven Raman-active modes ($4\,A_1' + 3E' + 4E''$) and six infrared-active modes ($3\,A_2'' + 3E'$). One of the Raman-active $3E'$ modes ($E'^{(2)}$) and acoustic mode $E'^{(1)}$ are counterparts of one of the six Davydov doublets. The remaining ten Raman-active modes ($4\,A_1' + 2E' + 4E''$) are components of five Davydov doublets (YOSHIDA et al.).

The symmetry coordinates found by Melvin projection operator method (MELVIN) were used to obtain the displacement vectors of atoms in all phonon modes of GaS and GaSe crystals. Figure 2 shows the atomic displacement vectors for Raman-active interlayer and intralayer modes. As seen from this figure, in these modes all the gallium and sulfur (selenium) atoms move either perpendicular or parallel to the layers.

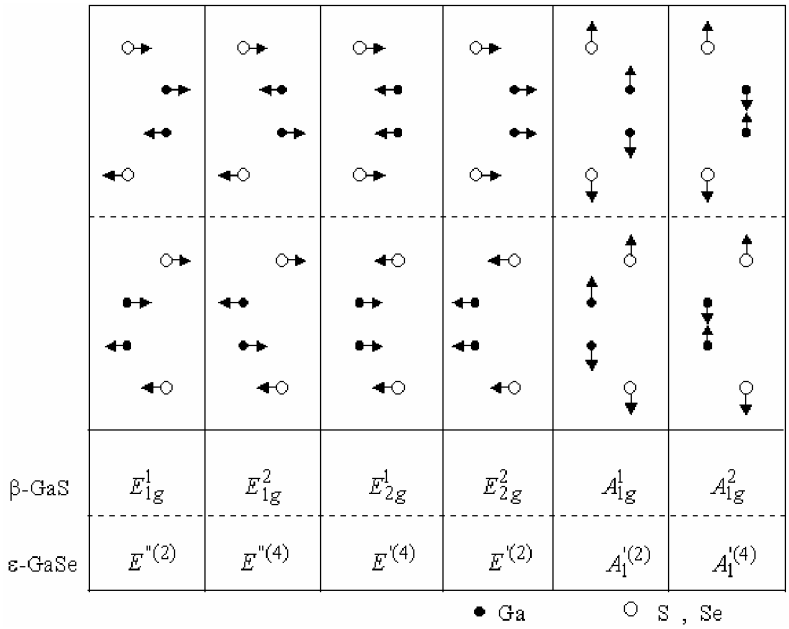

Fig. 2: Atomic displacement vectors for interlayer and intralayer Raman-active optical modes of β-GaS and ε-GaSe layered crystals.

3. Experimental details

Single crystals of $GaSe_xS_{1-x}$ were grown by Bridgman method. The analysis of X-ray diffraction data showed that they crystallize in a hexagonal unit cell. Crystals suitable for measurements were obtained by easy cleaving perpendicular to optical ***c***-axis. Raman scattering measurements were performed in the back-scattering geometry in the frequency

range 10-400 cm^{-1}. The 514.5 nm line of an argon laser and He-Ne laser (632.8 nm) were used as the exciting light sources. The scattered light was analyzed using a "Jobin Yvon" U-1000 double grating spectrometer and a cooled GaAs photomultiplier supplied with the standard photon counting electronics. The Raman line positions were determined within an accuracy of ± 0.1 cm^{-1}. A "CTI-Cryogenics M-22" closed cycle helium cryostat was used to cool the crystals from room temperature down to 10 K. The temperature was controlled within an accuracy of ± 0.5 K. In order to avoid sample-heating effects, we have chosen a cylindrical lens to focus the incident beam on the sample.

4. Results and discussion

Figure 3 represents the Raman spectra of $GaSe_xS_{1-x}$ mixed crystals at 10 K. These low-temperature measurements have demonstrated directly that all observed bands are due to one-phonon processes. Figure 4 shows the decomposition of the Raman spectra of $GaSe_{0.5}S_{0.5}$ crystal at the frequencies corresponding to the $A_1^{'(2)}$ (A_{1g}^1) intralayer compressional modes which have four distinct lines, two of which (A and D) are genetically related to the stretching vibration of atoms in the binary crystals GaSe and GaS, respectively, while the B and C lines have frequencies intermediate to A and D lines. Thus, in $GaSe_{0.5}S_{0.5}$ mixed crystal this stretching vibration of atoms shows a four-mode behavior. The dependencies of the frequencies of Raman-active modes on the compositions of $GaSe_xS_{1-x}$ mixed crystals are depicted in Fig. 5. One-mode behavior of interlayer $E^{'(2)}$(E_{2g}^2) and intralayer $E^{''(2)}$(E_{1g}^1) shear modes, and two-mode behavior of intralayer $E^{''(4)}$(E_{1g}^2) and $E^{'(4)}$(E_{2g}^1) shear modes, polarized along the layer, is in agreement with that of Ref. (HAYEK et al.; MERCIER, VOITCHOVSKY).

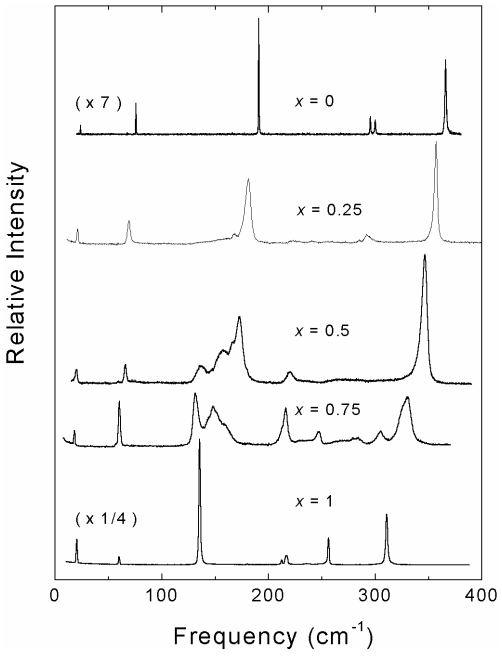

Fig. 3: Raman spectra of $GaSe_xS_{1-x}$ mixed crystals at T = 10 K.

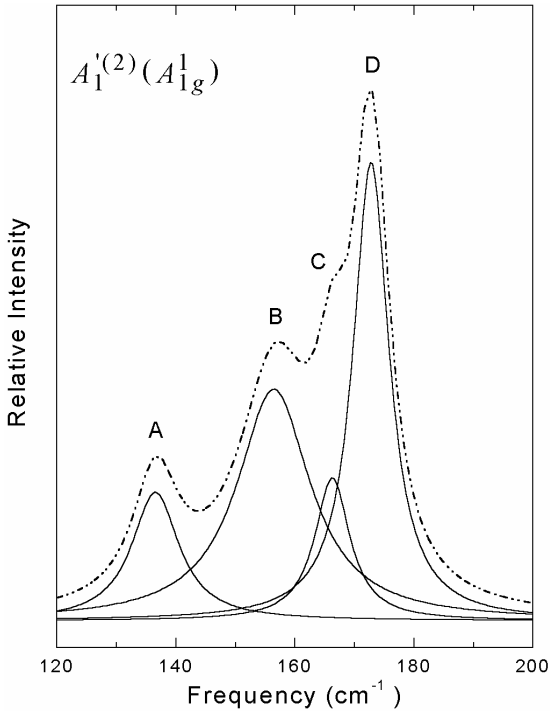

Fig. 4: The decomposition of the complex contour of the Raman-active $A_1^{(2)}(A_{1g}^1)$ compressional mode (dotted line) of $GaSe_{0.5}S_{0.5}$ mixed crystal into components.

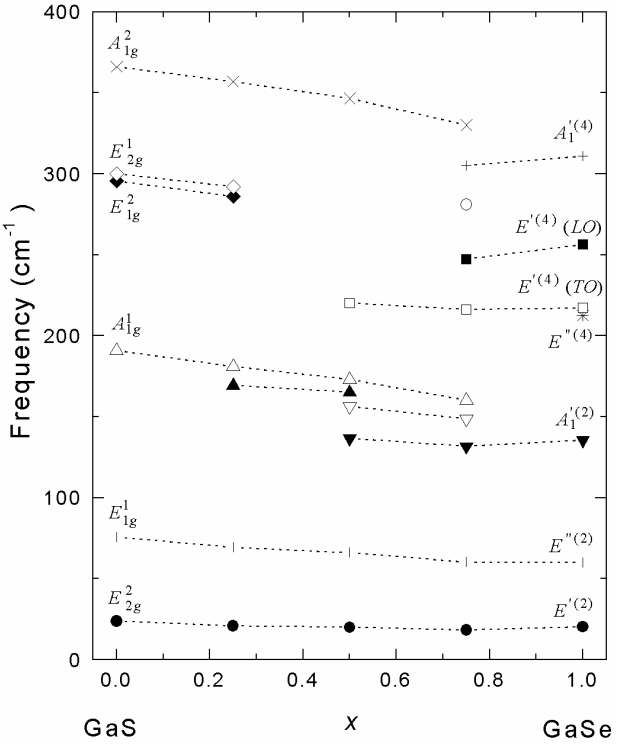

Fig. 5: Frequency dependencies of Raman-active modes on composition of $GaSe_xS_{1-x}$ mixed crystals.

Let us consider in detail the behavior of the intralayer compressional modes. The anisotropy of the crystal structure of $GaSe_xS_{1-x}$ leads to a perceptible difference in the dispersion in the Brillouin zone for intralayer shear and compressional modes polarized along and perpendicular to the layer, respectively. The rearrangement and the composition dependence of the intralayer mode frequencies in mixed crystals may be described by the cell isodisplacement model in some cases (ZINGER et al.; BARTA et al.). This model holds for modes with low dispersion in the Brillouin zone. Therefore, such a model may be applicable to the $A_1^{\prime(2)}$ (A_{1g}^1) and $A_1^{\prime(4)}$ (A_{1g}^2) intralayer compressional modes of the $GaSe_xS_{1-x}$ mixed crystal, polarized perpendicular to the layers (Fig. 2). These modes in GaSe and GaS layer crystals have very low dispersion in the Brillouin zone due to a weak interlayer interaction (JANDL et al.; POWELL et al.). Distinctly observed four-mode behavior in the Raman spectra of the $GaSe_{0.5}S_{0.5}$ mixed crystal for the $A_1^{\prime(2)}$ (A_{1g}^1) intralayer compressional mode (Figs. 3-5) may be explained by the cell isodisplacement model. Three different kinds of cell singled out in the layer of mixed crystal, namely, Se – Ga - Ga - Se, Se - Ga - Ga - S, and S - Ga - Ga - S, may be identified with a certain set of normal vibrations, corresponding to each cell. Mixed cells composed of Se - Ga - Ga - S can be formed during the growth of the crystals.

As stated above, the lines A and D are genetically related to the stretching vibration of atoms in binary crystals GaSe and GaS, respectively. The lines B and C associated with the mixed cells Se - Ga - Ga - S are expected to have different frequencies in different stacking configurations. The motion of the atoms in the mixed cells Se - Ga - Ga - S is perpendicular to the layers. A change of the interlayer interaction, due to a change in the stacking, affects the mode frequencies associated with the mixed cells. In $GaSe_{0.5}S_{0.5}$ mixed crystal, two stackings (ε- and β-polytypes) coexist and the B and C lines can be observed simultaneously. The arrangement of the adjacent layers in β-polytype is different from that in ε-polytype. This leads to an alignment of cations and anions such that an ionic contribution to the weak interlayer bonding results for the β-polytype (Fig. 1). The calculations with the linear chain model shows that interlayer compressional constant is about three times larger in β-stacking than in ε-stacking (MERCIER, VOITCHOVSKY). Therefore, we may assign B and C lines ($\nu_B < \nu_C$) in the Raman spectra of $GaSe_{0.5}S_{0.5}$ mixed crystal to vibration of atoms in the ε- and β-stackings, respectively.

The rearrangement behavior of high-frequency $A_1^{\prime(4)}$ (A_{1g}^2) compressional mode differs from the one-mode behavior reported earlier (HAYEK et al.; MERCIER, VOITCHOVSKY). In the Raman spectra of $GaSe_xS_{1-x}$ mixed crystals an unusual two-mode behavior is observed for this vibration (Figs. 3,5). The intensity of the line originating from stretching vibrations of atoms in the binary GaSe crystal decreases faster than that in binary GaS crystal. Therefore, in the Raman spectra from $GaSe_xS_{1-x}$ mixed crystals with $x < 0.75$ we observe in the 305-365 cm^{-1} range one line corresponding to the pure component GaS. Besides those two bands, a third additional band of low intensity is observed for $x = 0.75$, having a lower frequency than the above two bands. Similar unusual two-mode behavior has been predicted earlier for stretching mode ν_4 in $Hg_2(Cl_xBr_{1-x})_2$ chain mixed crystals (BARTA et al.). There, it was proposed that this additional band is due to complex relative motions of the atoms in disordered sublattices. With these vibrations, the change in the polarizibility is slight and they can appear in the Raman spectra as weak bands.

Different behavior of $A_1^{\prime(2)}$ (A_{1g}^1) and $A_1^{\prime(4)}$ (A_{1g}^2) compressional modes may be associated with the difference in sets of atomic displacements for these modes. For the $A_1^{\prime(2)}$ (A_{1g}^1) mode the restoring forces are due to strong intralayer gallium-gallium ($C_{Ga\text{-}Ga}$ = 108 and $C_{Ga\text{-}Ga}$ = 110 N/m for GaSe (WIETING) and GaS (LUCAZEAU), respectively) and weak interlayer selenium-selenium (sulfur-sulfur) ($C_{Se\text{-}Se}$ = 9.2 and $C_{S\text{-}S}$ = 9.5 N/m) bonds. In $A_1^{\prime(4)}$ (A_{1g}^2) mode, stronger intralayer gallium-selenium (sulfur) ($C_{Ga\text{-}Se}$ = 123 and $C_{Ga\text{-}S}$ = 130 N/m) bonds are also involved in restoring forces (Fig. 2). Here C is the compressional force constant associated with the relative displacements of the atomic planes. Thus, the frequency of the $A_1^{\prime(4)}$ (A_{1g}^2) mode is essentially determined by the relative motions of the atoms within one layer. Note that the intramolecular stretching mode ν_4 in $Hg_2(Cl_xBr_{1-x})_2$ mixed crystals also arises from the relative vibrations of both mercury-mercury and mercury-chlorine (bromine) atoms (BARTA et al.).

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